M. C. Sutherland
'52

MEMORANDUM

QXPA RESIN: PROGRAM OF ACTIVITIES IN PRODUCTION AUTOCLAVES

AUTHORS: J. F. Erdmann
R. C. Wise
J. C. Alexander

J. F. Erdmann,
Group Leader

DATE: February 14, 1961

FILE NO: B:20:835-M10

Project No.: 514X

Recent efforts to scale up the process for QXPA r sin from the E17 600-gallon Development autoclave to the C14 4600-gallon Production autoclave have been notably erratic and non-reproducible insofar as achieving the desired high density, smooth, bead-like particles necessary for producing low viscosity plastisols. The major defect in the recent unsatisfactory runs can be best described as incorrect particl geometry - instead of the smooth, spherical, glassy, fairly uniform beads of 60-80 microns median size, we have been making rough, cobbled, agglomerated particles of 150-200 microns or larger median size with a high percentage of fines. The agglomerated particles are usually glassy rather than porous in nature, and their appearance suggests that some factor early in the polymerization is causing agglomeration of the smooth beads at some later point in the process.

All runs to date have utilized a Pfaulder 56" diameter S.S. retreat-curve impeller set one-half its diameter (28") above the bottom of the autoclave. The autoclave has been baffled with 4 flat baffles, 5" wide x full straight side length, to produce a greater turn-over with less swirling vortex. The recipe used has contained CELLOSIZE QP-4400, sodium bicarbonate buffer, and DLP catalyst.

Variables studied in recent runs have been:

1) Monomer/water ratio - 30/70 to 35/65
2) Agitator speed - 90 to 120 rpm
3) Autoclave level - 50% and 75% full, to enable varying power per unit volume of charge (5.7 to 14.4 HP/1000 gallons)
4) CELLOSIZE concentration - 0.20 to 0.30%

DEVELOPMENT DEPARTMENT
UNION CARBIDE CHEMICALS COMPANY
SOUTH CHARLESTON, WEST VIRGINIA

5) Source of vinyl chloride - No. 2 pyrolysis and No. 3 synthesis systems
6) Different blends of CELLOSIZE - two blends have been used

No consistent pattern could be drawn from any of the runs in which these variables were controlled. However, certain facts became apparent -

1) The E17 600-gallon autoclave, with geometric similarity in agitator arrangement, and with raw mat rials and procedures commonly used in production, consistently produced a high quality QXPA resin.

2) The C14, 4600-gallon autoclave would not produce QXPA reproducibly under the conditions employed in th last 16 runs. Initially, most of these runs were made at the same conditions as the 600-gallon autoclave runs. A clear indication of why only 3 of th s C14 runs were successful and the others were not is the major problem we face at this time.

3) An examination of autoclave slurry samples taken periodically during past runs indicated that the "feel" of the resin could show whether a run would be good or bad. This difference in "feel" (smooth and creamy for good results, and grainy or stringy for poor results) was apparent in slurries taken as early as zero-hour or zero-hour + 1.

   This very crude test could tell us if the run would agglomerate and not form glassy beads, but did not give any indication of how good the resin might be if glassy beads resulted.

4) From these factors we believe that our troubles can be localized to this extent:

   a) A difference which is not readily apparent has existed in the C14 autoclave system compared to the E17 autoclave system
   b) The cause of the particle agglomeration is taking effect in the charging, heat-up, and very early stages of the operation. This suggests the following areas for investigation:

      1) Charging procedures, including methods of oxygen removal and merging of recipe components.
      2) Raw material quality, particularly monomer.
      3) Agitation differences, particularly time and space factors which cannot be avoided.

With these points in mind, a meeting of Development and Production personnel agreed on the following general approach to this problem:

1) An attempt to produce QXPA by means of the Mixco turbine agitation system and Elvanol E88H recipe used in C14 autoclave before Process-5 is highly desirable to help ease the pressure on this project from potential customers for QYNV and QXKV-2 resins with which sales of QXPA is related for certain applications.

2) Because of the delay necessary to locate and obtain the required gears, impellers, baffles, and other equipment for a change to the Mixco system, and because certain points about the present process had not been established, several additional runs would be made in C14 immediately with the CELLOSIZE recipe.

The following two-part program has therefore been established: first, the runs with Pfaudler agitation and the CELLOSIZE recipe, and second, the series with Mixco agitation and Elvanol recipe.

I. QXPA Series - Pfaudler agitation, CELLOSIZE QP-4400 recipe

Run No.	Autoclave Level-%	CELLOSIZE Conc.-%	Agit. rpm	Pre-mix P riod
C14-1-21	50	0.20	100	20°C, 2 hours
C14-2-22	50	0.20	75	20°C, 2 hours
C14-3-23	50	0.30	75	20°C, 2 hours

A. Oxygen concentrations in vapor phase before zero-hour to be less than 50 ppm as monitored by the new Analytic System Co. oxygen analyzer.

B. Vinyl chloride source to be constant, if at all possible. (No. 2 system, 5:1 reflux ratio on column.)

C. Make all three runs regardless of results of any on of them, before doing anything else.

D. Repeat successful runs exactly for ability to reproduce.

Conclusions and follow-up action on the basis of these three runs:

A. If all three runs are successful and are repeated successfully, our scale-up problems are greatly reduced. The provision of adequate pre-mix time will be the answer to previous failures. Conditions can be adjusted as required to produce the amount of resin desired for Technical Service commitments.

Further work would include repeating the first run at 75% level for increased productivity. Adjustment would be needed for control of particle size and density.

B. If only the first run is successful, we will know that our past work has been good, but over-ridden by the eff ct of inadequate mixing prior to polymerization. We will also know that 75 rpm is too slow, or that power equality must be maintained. This could lead to adding another impeller to the shaft or using a larger Pfaudler impeller.

Further work in this case would be to again try for the 75% level, but exercise care in adjusting agitator speeds because of lower limit.

C. If either the second or third run, or both, are successful, and the first run is not, the effect of agitation will be apparent. The pre-mix period will be of doubtful value, since the high agitation of the first run might be the deciding factor.

Further work here would be to repeat the better of the two runs using shorter mix periods to determine effect of the pre-mix period, if it exists. Otherwise, adjust speeds and recipe to get optimum results.

D. If none of the runs are successful, the effects of agitator speed, pre-mix period, and CELLOSIZE concentration would all be considered insufficient to overcome the real problem, which would remain unidentified unless ferreted out from analytical data obtained during the series.

Follow-up on this would be to convert the autoclave immediately to Mixco impellers and the use of the Elvanol recipe to attempt duplication of QXPA resin QEX-0125.

Additional work might be considered for E17 or E8 autoclaves to gain more information for comparison with our C14 experience.

II. QXPA Series - Mixco Agitation, Elvanol E88H recipe (QEX-0125).

Run No.	Autoclave Level-%	Elvanol Conc.-%	Agitation rpm*	Pre-mix Period
1 (0124)	95	0.30	40	20°C, 20 min.
2 (0125)	95	0.30	37	20°C, 20 min.
3 (0126)	95	0.35	37	20°C, 20 min.
4	95	0.35	35	20°C, 20 min.

* Two 48" Mixco impellers, 4, 9" flat baffles.

A. Monomer/water ratio = 30/70, sodium bicarbonate conc. = 0.05%, trichloroethylene concentration = 0.5%, t mperature = 57°C, all conditions same as for QEX-0125.

B. Make all runs regardless of results of previous runs (except for setting up a run solid).

C. Repeat successful runs exactly for reproducibility.

D. Procedure for operation - Monomer, trichloroethyl ne, and catalyst charged first to C14 at 20°C. Water, E88H, and sodium bicarbonate to be mixed in C19 at 20°C. C19 to be purged twice to 35 psig and vented to remove oxygen. Transfer C19 contents to C14 at 20°C, venting C14 at same time to purge oxygen (reverse charge, cold). Stated mix period and agitation to be provided, followed by heat up to operating temperature.

Conclusions and follow-up on basis of these four runs:

A. If all runs are successful, we have reproduced QEX-0125 results, and we have shown that reverse charge cold is workable. Slight adjustments may be required for best resin properties.

Follow-up to this would be to attempt present charging procedure to determine need for retaining the more complicated procedure. A switch from Elvanol to CELLOSIZE would be appropriate, if conditions permit. Otherwis , adjust process for best resin properties. A study of effect of TERGITOL NPX addition for tensile improvement of fused plastisol films would be in order.

B If Runs 1 or 4, or both, fail, but runs 2 and 3 ar successful, the process has still been reproduced adequately. We may have a very sensitive process on our hands; therefore, some care in operations appears justified.

Follow-up to determine reason for sensitivity. Incr ase mix period time for maximum stability. Hold to best conditions for several runs to see how reproducible th operations will be, and to determine if possible whether sensitivity is related to our previous troubles with the Pfaudler system.

C. If all four runs fail, we probably have the same causes to blame as in the Pfaudler system. The first item to check would be monomer quality. This ties in with the Pantasote problem and could probably be considered a part of it, until proven otherwise.

Follow-up to this would be to look into longer mix period or return to exact QEX-0125 procedures, but chances of success at this stage appear poor. At this point, a return to the analytical results and attempts to measure and correlate physical properties in the suspension system appear justified, along with an attempt to tie these efforts to monomer quality.

III. In both series of runs, the following special efforts will be made:

A. Review all instructions and procedures, and data sheets, etc. Revise as necessary.

B. Oxygen analyses for each run. Do not conduct run with O_2 greater than 50 ppm. Test value of venting and/or evacuation by frequent analyses during the procedure.

C. VCl quality -- take VCl sample from feed line before each run. Hold for possible check runs in bombs.

D. H_2O quality -- take H_2O sample during charging. Run "Tropfenzahl" and hold for further analysis.

E. CELLOSIZE quality -- sample mix as charged to autoclave. Test for gels and insolubles. "Tropfenzahl" if possible. Evaporate to dryness for total solids determination.

F. Mischarges -- sample aqueous portion of charge just before VCl addition. Tests: Gels, insoluble, "Tropfenzahl", total solids.

G. VCl samples from stripping at end of run (for VCl problem).

H. Samples during run

1. After VCl is added, sample aqueous phase at start and at end of mixing period.

2. Sample every half hour during warm-up and through second hour after zero-hour ("Tropfenzahl", pH).

3. Autoclave slurry hourly after second hour ("Tropfenzahl", pH).

DISTRIBUTION

Mr. D. W. Finn, 514
Mr. J. E. Deitzler, 514
Mr. M. E. Sutherland, 514
Mr. G. J. Hanks, Jr., 514
Mr. G. E. Brant, 514
Mr. J. L. Johnson, 514
Mr. M. W. Jones, 514

Dr. J. J. Brezinski
Mr. D. L. Engle
Mr. W. S. Engle
Mr. A. E. Montagna
Mr. H. E. Persinger
Mr. C. R. Welter
Mr. W. E. Whitehurst